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Reaction Between Thin Gold Wires and Pb-Sn-In Solder (37.5%, 37.5%, 25%), Part A: The Radial Reaction Inside The Solder Mounds, Its Linear Reaction Model, Statistical Variation of Reaction Rate, and Induced Structural Changes In The Solder Mounds.

W. J. Siekhaus

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Disclaimer

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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A.I.) Introduction

Thermodynamics favors the reaction between indium and gold, since the heat of formation of $AuIn_2$ is 6 kcal/mole[1], substantially larger than the heat of formation of any other possible reaction product. Thermodynamic equilibrium between gold and the elements in the solder mound is reached only when ALL gold is converted to $AuIn_2$. There are two aspects to this conversion: A) the reaction WITHIN the solder mound (called here "radial reaction") and B) the reaction OUTSIDE the solder mound (called here "axial reaction") and the transition from A) to B).

[1] Hultgren, R.R. Selected values of the thermodynamic properties of binary alloys. ASM 1973, Metals Park, OH.

The reaction between thin gold detonator wires and the In/Pb/Sn solder mound in older detonators has been looked at repeatedly [2],[3],[4],[5],[6],[7]. There are, in addition, two studies which look at the reaction between indium and gold in planar geometry [8],[9]. All data are shown in tables I to V below.

It is the objective of this section dealing with aspect A), to combine all of these results into a reaction model and to use this reaction model to reliably and conservatively predict the gold-solder reaction rate of soldered gold bridge-wires as a function of storage temperature and time.

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[2] Braun, J. D., Rhinehammer T. B. (1963). "An Investigation of the Reaction between Pure Gold Wire and Lead Tine Indium Solder." Transactions ASM **56**(4): 870-874.

[3] Janco, B.L., Braun, T. D. "Investigation of the Reaction Rate Between Pure Gold and Pb-Sn-In Solder", Monsanto Report (Mound Laboratory).

[4] Harwood, W. D., "Effects of Gold-Indium Diffusion on Bridgewires in EBW Detonators B28, W30, W31, W45, W53", Quality Eng. Reprt Dec. 16, 1977, Sandia National Laboratory, Albuquerque, NM

[5] Harwood, W.D., "Dissection Analysis of MC1240 Explosive Shaped Charge – W45", Quality Eng. Report, Jan. 23, 1978, Sandia National Laboratory, Albuquerque, NM.

[6] Siekhaus, W. J. "Statistical Analysis of Gold-Bridge-Wire Dissolution in Detonators at Storage Temperature", UCRL 83438, Dec. 1979.

[7] Folkers, C., Griffith, C. "Reaction of Gold Wires of Various Diameters at 80°C With Pure Indium and In/Sn/Pb (25, 37.5, 37.5) Solder and 120°C". Internal Memorandum, LLNL, Nov. 1980.

[8] Powell, G. W. and J. D. Braun (1964). "Diffusion in Gold-Indium System." Transactions of the Metallurgical Society of AIME **230**(4): 694-&.

[9] Yost, F. G. G. F., KARNOWSKY MM (1976). "LAYER GROWTH IN AU-PB-IN SOLDER JOINTS." METALLURGICAL TRANSACTIONS A-PHYSICAL METALLURGY AND MATERIALS SCIENCE **7**(8): 1141-1148.

TABLE 1. PLANAR REACTION KINETICS

Data of W. Powell and T. Braun[7]

	T = 142°C, 415 K, $\frac{1}{T} = 2.41 \times 10^{-3} (\frac{1}{K})$			T = 151°C, 424 K, $\frac{1}{T} = 2.34 \times 10^{-3} (\frac{1}{K})$		
Reaction time hours months	144 0.20	474 0.658	1056 1.467	100 0.139	336 0.467	504 0.7
Reaction Product Thickness, μm						
$Au\ In_2$ layer	61	127	158	92	157	218
Gold equivalent* of $In_2\ Au$ layer	14.52	30.24	37.62	21.9	37.38	51.9
Au In, $Au_9\ In_4$ $An_4\ In$ layer	11	22	32	11	23	28
Gold equivalent†	4.3	8.7	12.6	4.33	9.1	11.01
Total reaction layer, Gold equivalent	18.8	38.9	50.22	26.2	46.5	62.9

*$Au\ In_2$ layer divided by 4.2

$$4.2 = \frac{\text{cm}^3/\text{gold atom in Au In}_2}{\text{cm}^3/\text{gold atom in Au}} = \frac{\frac{42.8\ \text{cm}^3}{\text{mole Au In}_2}}{\frac{10.2\ \text{cm}^3}{\text{mole Au}}}$$

† Layer is mostly Au In. Layer divided by

$$2.54 = \frac{\frac{15.7\ \text{cm}^3}{\text{mole In}} + \frac{10.2\ \text{cm}^3}{\text{mole Au}}}{\frac{10.2\ \text{cm}^3}{\text{mole Au}}}$$

Table II. Layer Growth Reaction Kinetics, Planar Geometry

(Yost et al)

70°C				85°C				100°C			
d'(μm)	d(μm)	t'(m)	t(h)	d'(μm)	d(μm)	t'(m)	t(h)	d'(μm)	d(μm)	t'(m)	t(h)
.59	3.2	.067	48.0	.024	2.9	.042	30.2	.24	3.8	.034	25.0
.41	4.5	.133	96.0	.118	3.3	.056	40.0	1.03	7.1	.069	50.0
.48	4.8	.233	168.0	.18	3.6	.069	50.0	1.36	8.5	.104	75.0
1.42	8.8	.70	504.0	.48	4.8	.091	65.3	2.31	12.5	.14	101.5
1.76	9.5	.93	672.0	.68	5.7	.11	80.0	2.83	14.7	.21	150.0
2.23	12.2	1.17	840.0	.81	6.2	.14	100.0				
2.96	15.0	1.4	1008.0	.98	6.9	.194	140.0				
				1.39	8.6	.298	215.0				
				2.2	12.1	.43	310.0				

110°C				120°C				130°C			
d'(μm)	d(μm)	t'(m)	t(h)	d'(μm)	d(μm)	t'(m)	t(h)	d'(μm)	d(μm)	t'(m)	t(h)
.194	3.6	.011	8.0	.69	5.7	.0125	9.0	.41	4.5	.0042	3.0
.26	3.9	.015	11.0	2.36	12.7	.042	30.0	.33	4.2	.0046	3.3
.65	5.5	.022	16.0	3.88	18.9	.069	50.0	.67	5.6	.0056	4.0
.76	6.0	.028	20.5	5.54	26.3	.104	75.0	.998	7.0	.0083	6.0
1.02	7.1	.042	30.0	14.9	65.8	.278	200.0	1.02	7.1	.011	8.0
1.42	8.8	.056	40.0					1.39	8.6	.014	10.0
1.75	10.2	.069	50.0					1.75	10.2	.021	15.3
2.32	12.6	.090	65.0					3.39	17.0	.035	25.0
2.81	14.6	.11	80.0					5.8	27.1	.069	50.0
								7.8	35.6	.104	75.0
								10.6	47.5	.139	100.0

Table II. Layer Growth Reaction Kinetics, Planar Geometry (cont'd)

140°C				150°C				160°C			
d'* (μm)	d (μm)	t' (m)	t (h)	d'* (μm)	d (μm)	t' (m)	t (h)	d'* (μm)	d (μm)	t' (m)	t (h)
.21	3.7	.0028	2.0	.55	5.1	.0032	2.3	.68	5.7	.0028	2.0
.84	6.4	.0046	3.3	.92	6.7	.0046	3.3	.72	5.8	.0028	2.0
1.14	7.6	.0075	5.4	1.02	7.1		4.0	1.12	7.8	.0042	3.0
4.06	20.3	.028	20.0	.95	10.2	.0083	6.0	1.35	8.5	.0046	3.3
3.04	26.4	.042	30.0	1.76	13.7	.014	10.0	1.8	10.3	.0053	3.8
5.62	32.5	.056	40.0					2.33	12.6	.0069	5.0
								2.33	12.6	.0083	6.0
								2.72	14.2	.0097	7.0
								2.96	15.2	.0097	7.0
								3.5	17.8	.0125	9.0
								3.81	18.8	.014	10.0
								7.82	35.6	.028	20.0

170 °C			
d'* (μm)	d (μm)	t' (m)	t (h)
1.26	8.1	.0025	1.8
1.77	10.3	.0035	2.5
2.09	11.6	.0044	3.2
2.42	13.0	.0049	3.5
2.55	13.5	.0056	4.0
3.32	16.8	.0069	5.0
4.8	23.5	.011	8.0
5.73	26.7	.014	10.0

d_0= 2.8 μm

d'* = $(d-d_0)/4.2$ See * in table I

d_0 = 2.8 μm, average reaction layer formed during soldering, 250°C, 5 sec.

>>> d_0 = 2.8 μm isderived by plotting the data in table II, d′ versus time, fitting a linear equation to each set of data, and averaging their intercepts. See plots in reference [9] above, Yost et al.

Table III Circular Geometry
Initial Gold Wire Radius 19.05 μm
Data of J. D. Braun and T. B. Rhinehammer

	Temperature, C					
	50	60	70	80	100	120
Exposure Time Month	Decrease in Goldwire Radius, μm					
1	0	0	.683	1.98	3.97	6.06
2		.683	2.32	3.72	6.36	9.33
3	.27	1.32	3.43	5.08		11.3
3.5						12.7
4		1.79	4.31	6.26	9.39	14.5
5	1.03			6.88	11.2	19.05
6		3.47	6.31	8.88	12.9	
7		3.97			14.3	
8	1.46	4.4		10.4	19.05	
10	2.28	5.53	8.57	13.3		
11		6.16				
12			10.4	15.0		
16	4.05					
18		6.56				
33	6.06					

Table IV Circular Geometry
Data of B. L. Janco and T. D. Braun

Temperature C	Exposure Time, Month	Initial Wire Radius μm	% Au Consumed	Decrease in Gold-wire Radius, μm	Sample Size
17	0	19.05	0	0	1
100	1	19.05	36	3.81	1
100	2	19.05	56	6.41	1
54	24	19.05	72	8.97	1
17	96	8.9	40	2.00	3
17	108	10.16	47	2.76	4
17	108	8.9	48	2.48	6
17	132	8.9	53	2.8	3

Table V. Circular Geometry
Data of M. J. A. Gould, AWRE

Temp.	Exposure Time, Month	Initial Wire Radius, μ	ΔR, Decrease in Goldwire Radius	ΔR, Average in Goldwire Radius, μ
40-45 C Diurnal cycle	24	15.24	4.24, 4.24, 3.24, 3.24, 3.24, 4.24, 4.74, 4.24, 4.24, 4.24, 3.73, 4.74, 3.73, 3.24, 5.25, 6.24, 6.24, 3.73, 3.73	4.24 ± .9
	48	15.24	5.74, 8.24, 5.25, 10.24, 9.74, 12.24, 9.74, 8.74, 8.24, 11.73, 10.74, 11.73, 11.73, 5.74, 10.24	9.34 ± 2.31
	24	19.05	4.08, 5.74, 2.72, 3.63, 7.25, 2.41, 3.18, 3.94, 4.69, 3.33, 3.02	4.00 ± 1.43
	48	19.05	9.68, 10.58, 9.98, 9.98, 5.14, 6.81, 16.33, 4.99, 4.38, 9.37, 9.68, 5.74, 7.56, 10.29, 11.19, 7.25, 11.94, 10.58, 7.56, 7.11	8.81 ± 2.85
29 C	72	19.05	3.49, 2.54, 4.45, 2.06, 2.86, 1.91, 3.49, 4.28, 2.86, 3.18, 2.54, 3.18, 3.64	3.11 ± .77
20 C	118	19.05	3.02, 3.02, 1.66, 3.63, 4.53	3.17 ± 1.07

A.II.) Discussion of experimental data ("Radial" Reaction)

Gold reacts with Indium to form Gold-Indide ($AuIn_2$). Tables I to IV list in tabular form the thickness of Au converted as a function of temperature and time. Whenever the experimenters listed the thickness of gold-indide formed rather than the thickness of gold converted, the data were corrected using the formula given with each table. Figure 1 shows a plot of all data, for reaction in planar as well as in cylindrical geometry. The rate-limiting step in the formation of gold indide is not clear. The formation rate of gold-indide may be controlled by the interface between the old phases and the new phase ($AuIn_2$) being formed, or it may be controlled by the diffusion of one of the reactants. (Thermodynamic equilibrium requires that all the phases appearing in the phase diagram (see reference [1]) also appear in the reaction layer. However, they are so thin in this case that they are not detectable.) If the reaction is interface-controlled, it will proceed - in all geometries - linearly with time. If the reaction is diffusion-controlled, it will proceed in all geometries proportional to the square root of time [10]. Figure 1 shows that certainly for gold consumed in the range below 10 micrometer the overwhelming majority of data displays a linear dependence with time, independent of reaction temperature, and independent of geometry. Moreover the reaction rate at 70 C for a lead/indium (50/50) solder in planar geometry is the same as the reaction rate for the lead/tin/indium (37.5/37.5/25) solder in cylindrical geometry. It is ***very unlikely*** that this would occur if diffusion were a controlling factor. However, in experiments by Powell and Braun in planar geometry in which more that 10-micrometer gold is reacted, the data show a dependence on the square root of time. The data of Braun and Rhinehammer and Janco and Braun in cylindrical geometry also deviate from linear behavior when

[10] Diffusion, W. Jose and K. Hauffe, Steinkopf Verlag, Darmstadt 1982

more than 10µm of gold is reacted. It is entirely possible that the reaction becomes diffusion controlled as the thickness of the gold-indide increases, since indium has to diffuse through this layer to reach the gold surface. A "diffusion controlled model" will be developed later. The fact that this transition from interface controlled to diffusion controlled occurs independent of temperature at about 10 micrometer gold consumed implies that the activation energies for diffusion and for interface reaction have about the same value. The mathematical model used by Braun and Rhinehammer and by Janco and Braun to describe their data is not appropriate for a reaction-diffusion or an interface controlled mechanism. Siekhaus (see reference [7]) has attempted to use the large body of disassembly data to decide whether the reaction close to room temperature proceeds proportional to time or proportional to square root of time and has concluded that the available data do not allow to clearly differentiate between the two models. Since the concern here is not an academic one, but rather lifetime prediction, and since the majority of *very carefully* analyzed data (Yost et al.) support the conservative choice (reaction proportional to time) we will first develop a linear reaction model. A diffusion controlled model for gold consumption above 10 µm will be developed later.

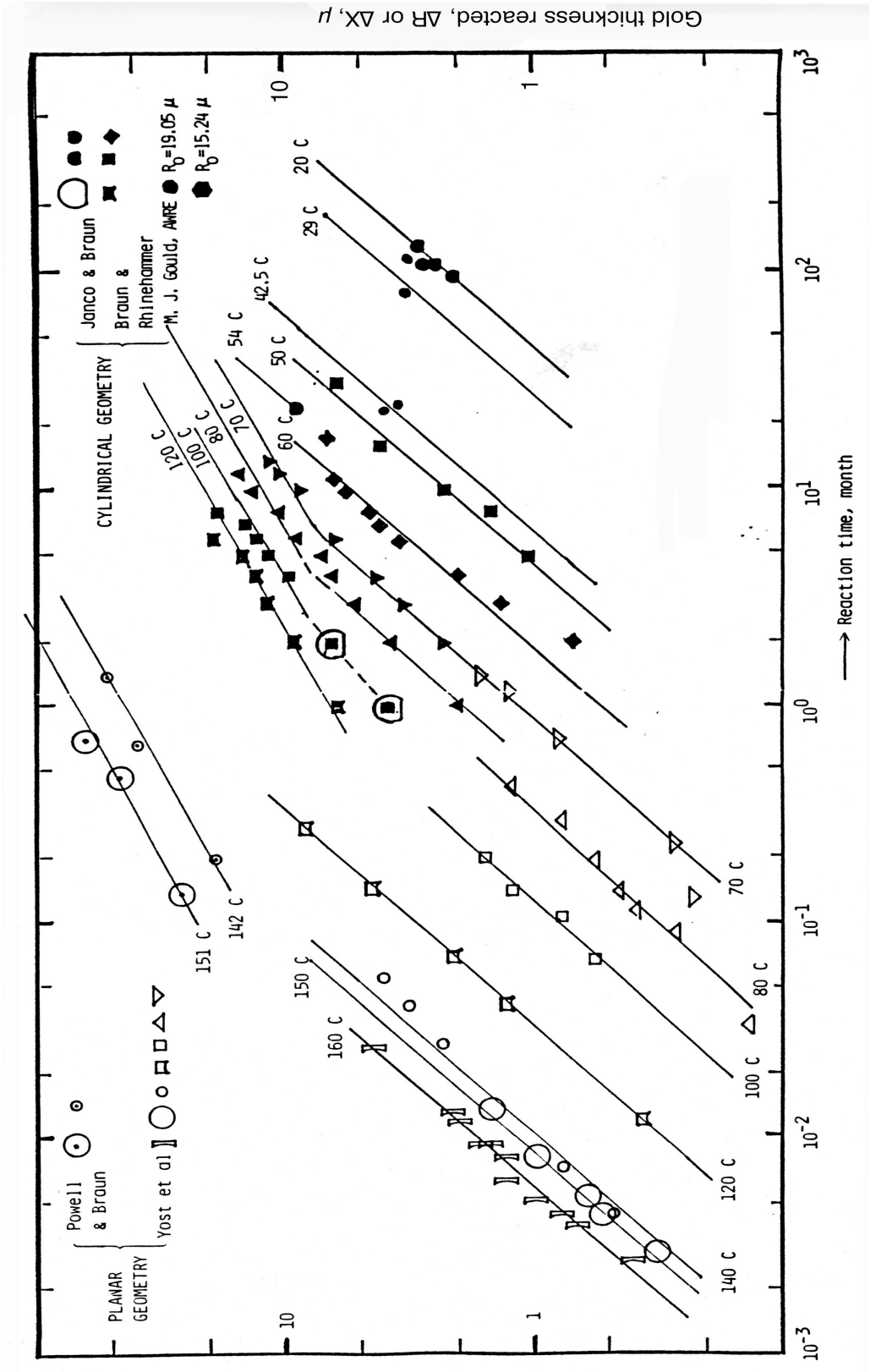

Figure 1. All experimental data.

A.III.) Linear radial reaction model and lifetime prediction for gold wires of 38.1µm diameter.

In Figure 2 we plot the thickness of gold reacted in one month as a function of 1/T. We use the slopes of the curve-fits (µm/month) in figure 1 to the data points $\Delta R \leq 10\mu m$ of Rhinehammer and Braun up to and including 70 C and the data of Yost el al. at and above 70 C up to 100 C. All the slope data fall reasonably well on a straight line, and a least squares fit gives us the activation energy of the reaction, as written down on Figure 2.

We define: Thickness of gold reacted = b * time

With $b = b_0 \exp -k/T$, $b_0 = 1.45*10^{10}$ µm/month, k = 7990 (K)

Yost et al. (Ref. [9] above) has an almost identical formula for the gold-indium reaction in *planar* geometry, even though the solder is NOT PbSnIn, but rather PbIn (50%,50%); the linear fit is still perfect for ΔX=15 µm, see his figure 12, 130°C. Yost's equation describes the thickness of the $AuIn_2$ layer, and its values are therefore a factor 4.2 higher, see the "* text" in table I. Our formula is used in figure 2 to calculate the amount of time needed at a given temperature T to convert a thickness ΔR of gold into $AuIn_s$. Three lines are drawn: ΔR=10, ΔR=15 and ΔR = 19.05 µm. The latter line depicts when a gold wire of 1.5 mil diameter is completely converted to $AuIn_2$. As an example: at 20°C 19.05 micrometer of gold will be completely converted in 900 month, at 35°C in 240 month. "Converted" means, of course, converted on the average.

Recognize that in the formula above, and in figure 2 we have extended the linear reaction model beyond the range ΔR or $\Delta X \leq 10\mu m$ where figure 1 clearly shows data to be linear with time. (Yost [9] shows linear behavior up to Δx=15µm). Thus we could OVERESTIMATE the rate of gold conversion above ΔR or $\Delta X \geq 10\mu m$. As stated above, this is being "conservative".

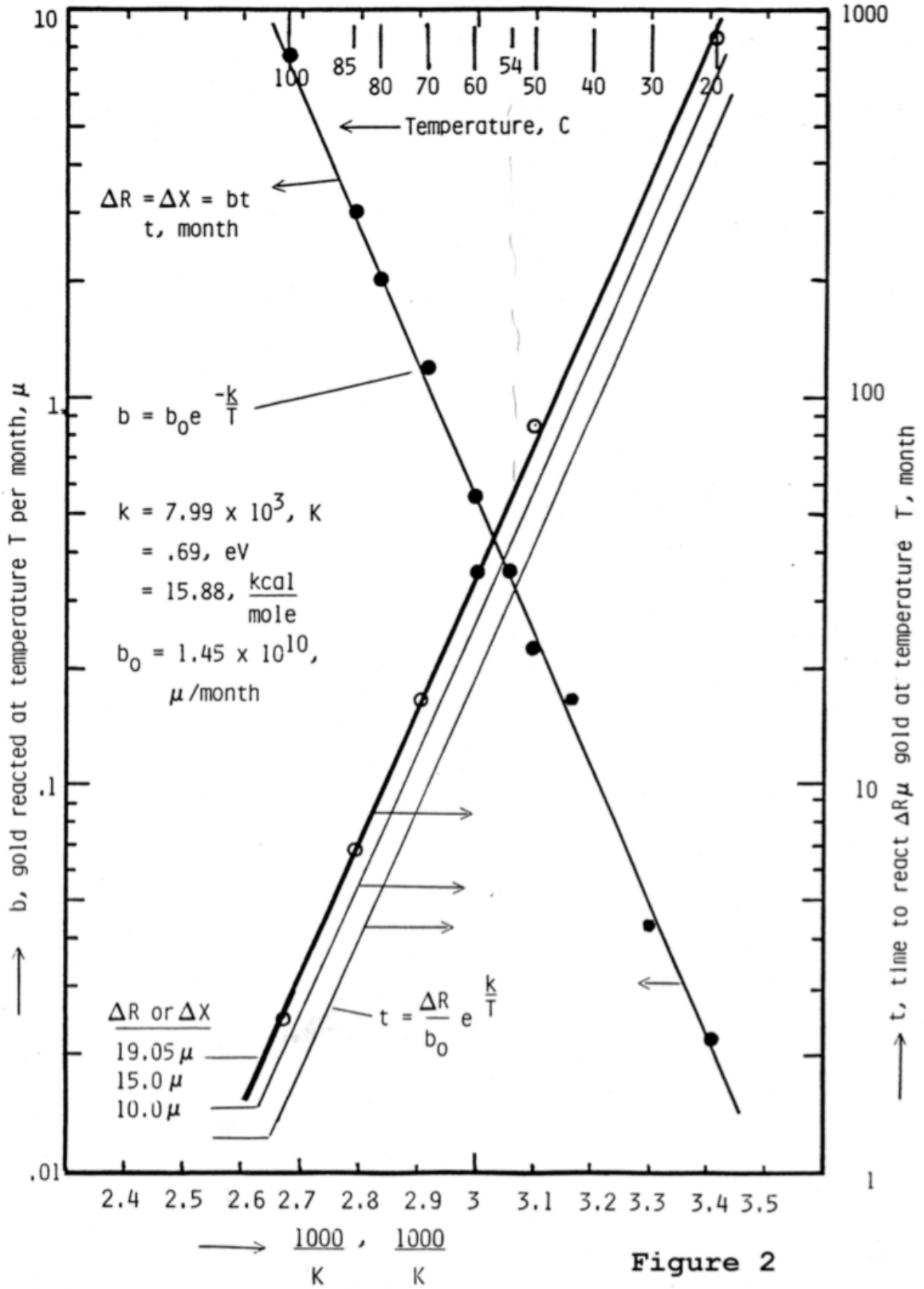

Figure 2. Formula and graph of the "linear reaction model".

A.IV.) Statistical variation in the $AuIn_2$ reaction.

Every natural process shows statistical variation. If we look at the probability distribution of bridge-wire consumption for a group of detonators sitting at 34.6 C for 123.5 month (Figure 3, "probability graph") we find a statistical distribution, which can be approximated by a Gaussian distribution, (straight line in figure 3), albeit with a lot of scatter around the line. This "straight line fit" produces an average gold wire radius decrease ΔR_0 of 8.73 μm (± 1.105 μm), while the equation of section III predicts ΔR = 9.38μM, reasonably consistent, since the temperature of 34.6 is not necessarily completely accurate, or constant over the 123.5 month. The slope of the line is related to the width of the Gaussian distribution: the smaller the slope, the wider the distribution). We assume (since we have no other knowledge) that the ratio of the standard deviation to the average stays constant with time, and project (Figure 4) that 50% of all soldered bridge-wires will have zero gold wire left after approximately 250 month, and that 2% of a population of bridge-wires will have no gold wire left in the solder mound after approximately 190 month (as indicated in Figure 4, approximately 1 micrometer of gold wire is frequently consumed during storage at lower temperature before a device is assembled). Figure 5 shows the distribution of gold wire consumption for 1.5 mil detonators held at 22.6 C. The distribution is narrower (steeper straight line), the average wire consumption, ΔR_o, is 4.35 ±.34 μm, while the linear model predicts 3.4 μm (consistent if one assumes that some gold conversion happens during initial soldering). Figure 6 shows the corresponding lifetime prediction. (A 50th percentile curve is also shown for bridge-wires at 20 C).

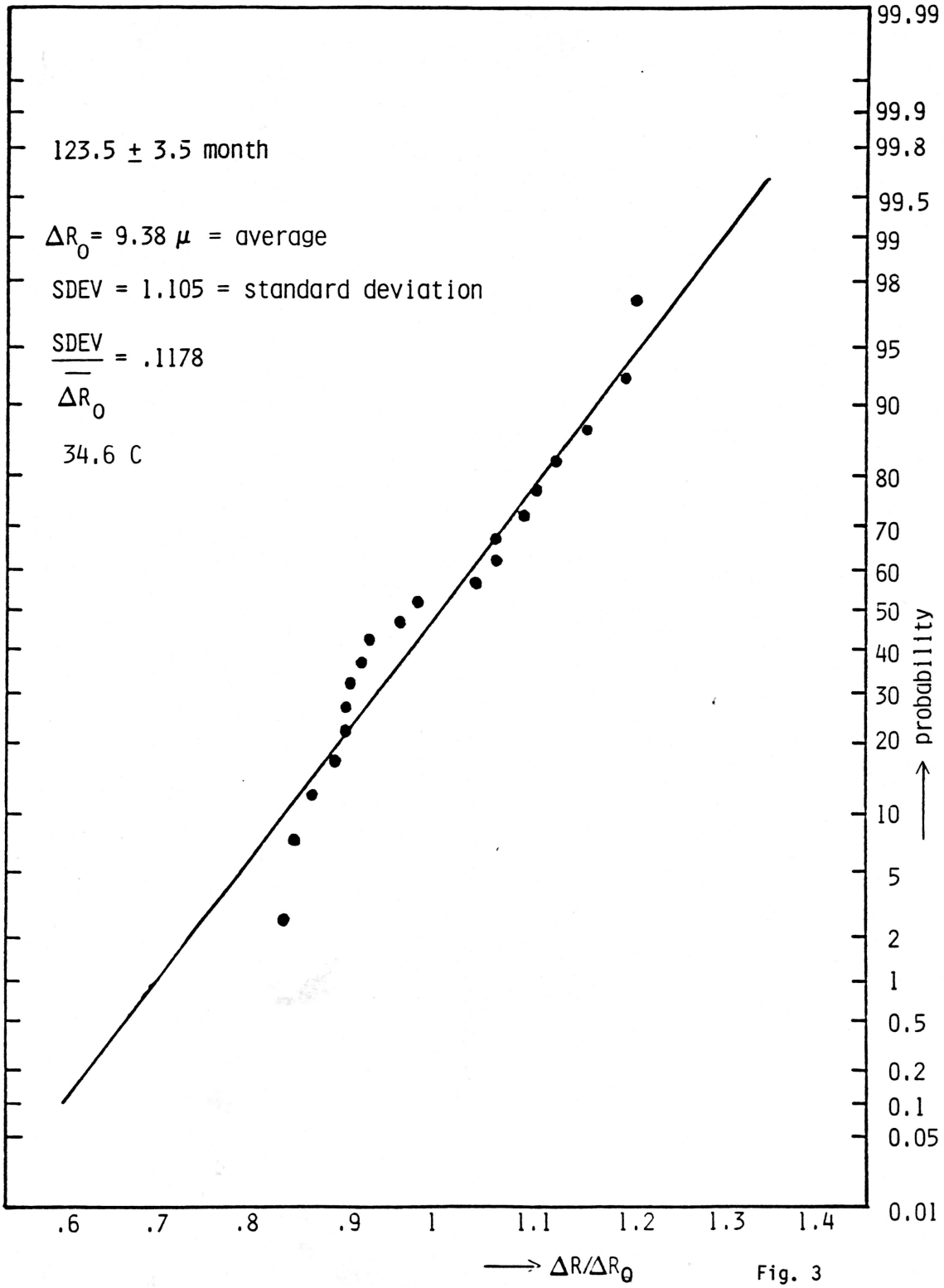

Figure 3. Probability distribution of gold consumption in soldered gold bridge-wires held at 34.6°c for 123.5 month.

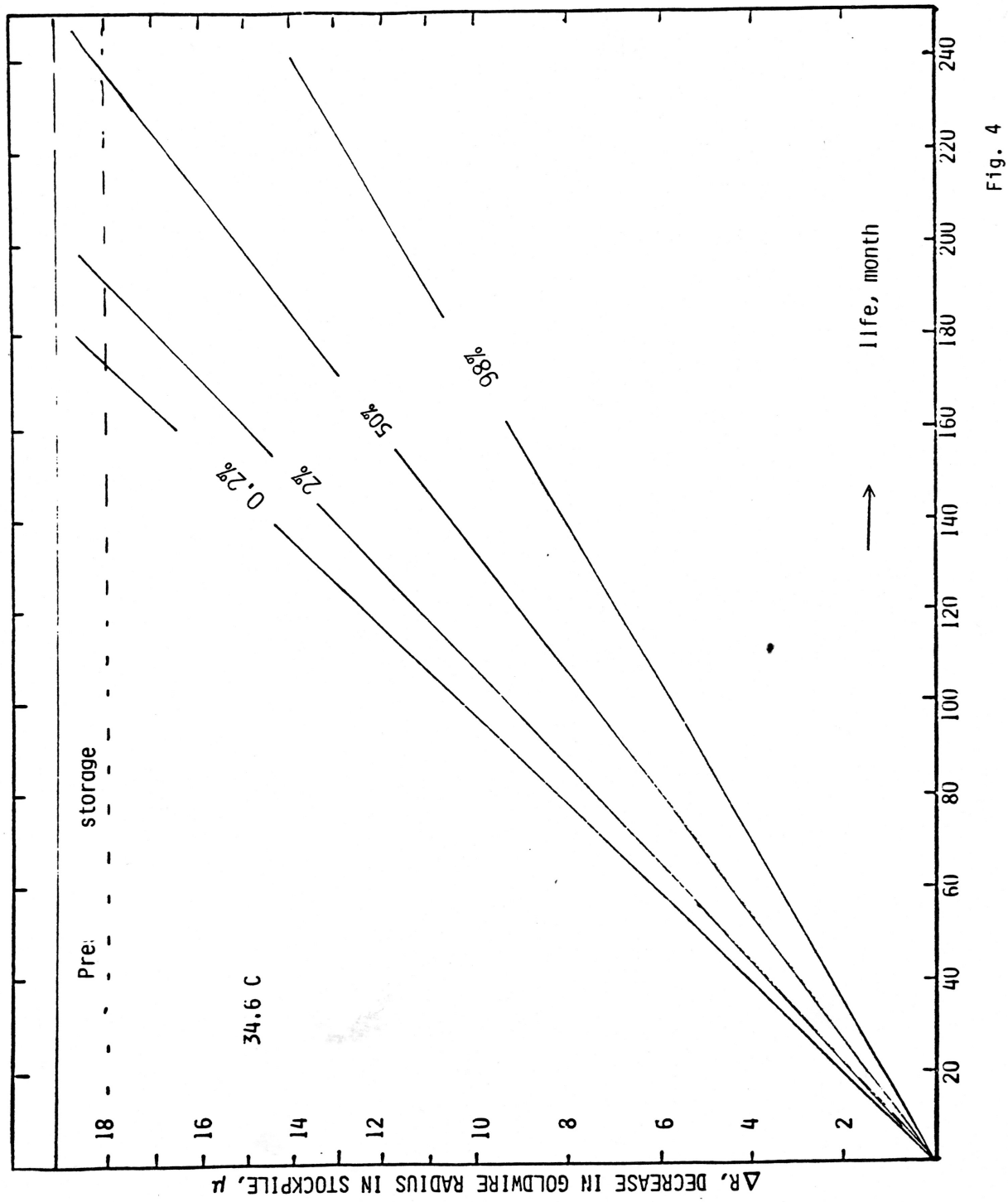

Fig. 4

Figure 4. Extrapolation of the probability distribution of gold consumption seen in figure 3 (held at 34.6°C for 123 month), showing the time when 0.2, 2, 50 and 98 percent of the soldered gold bridge-wires will be completely consumed.

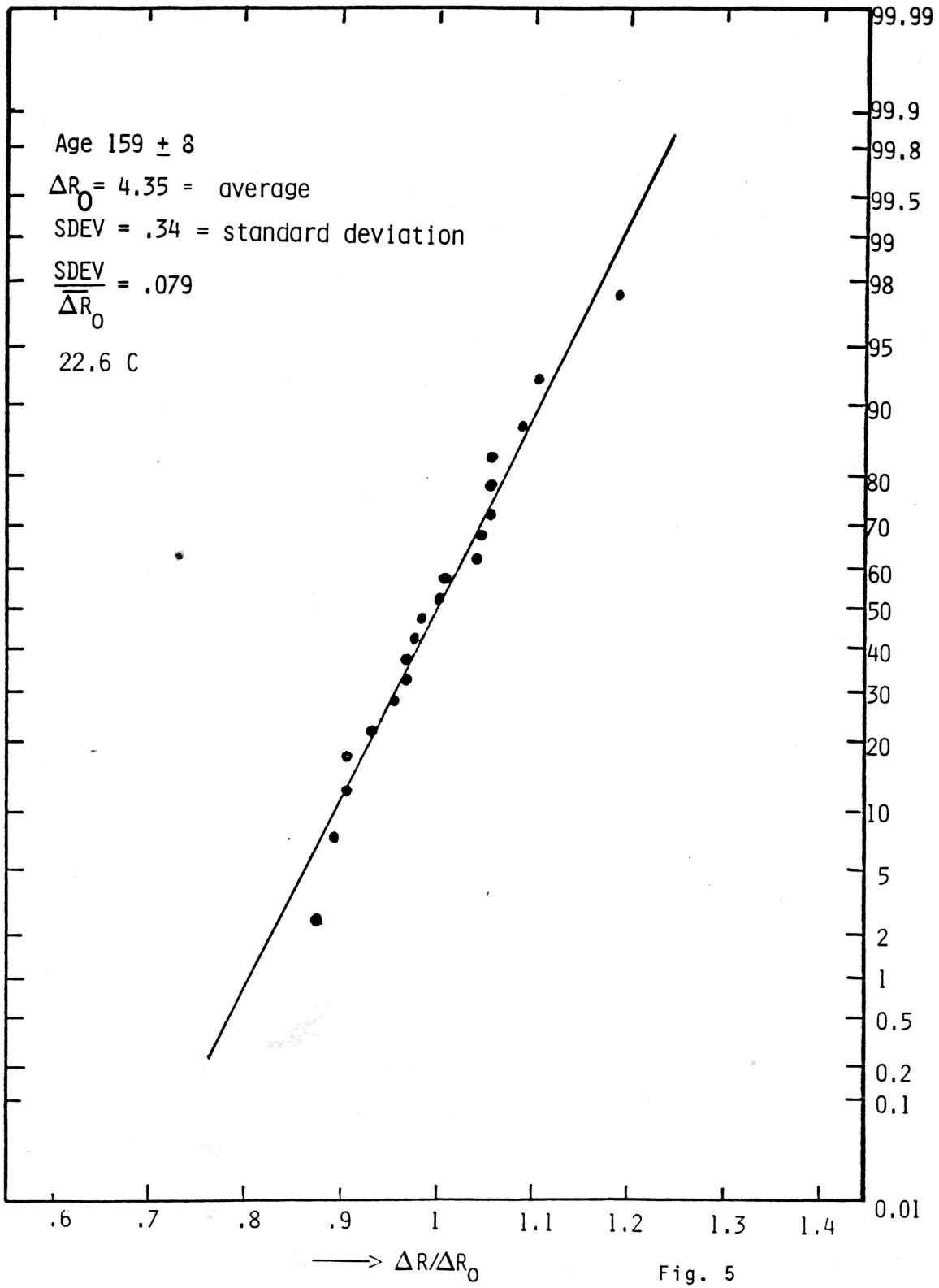

Fig. 5

Figure 5. Probability distribution of gold consumption in soldered gold bridge-wires held at 22.6°c for 159± 8 month.

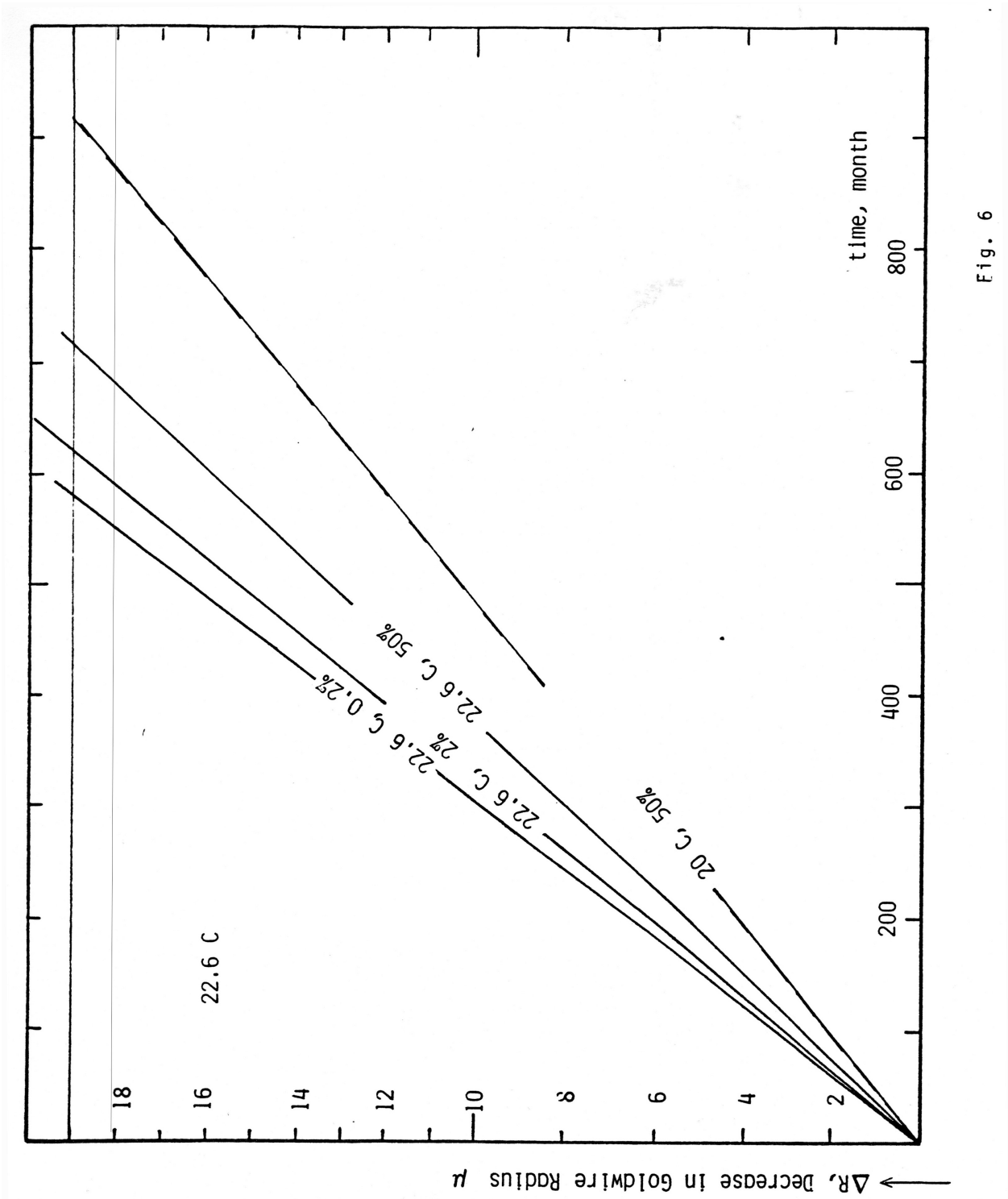

Fig. 6

Figure 6. Extrapolation of the probability distribution of gold consumption seen in figure 5 (held at 22.6°C for 159 month), showing the time when 0.2, 2, 50 and 98 percent of the soldered gold bridge-wires will be completely consumed.

A.V.) Structural changes associated with the "radial reaction".

The gold wire is typically held close to the surface of the header as it is being soldered. As the gold-indide layer grows concentrically around the wire, see figure 7, it pushes the center of the wire up, away from the 'base" (i.e. the copper/beryllium pin to which it is soldered), in the process moving the solder's lead and tin out of the way everywhere. This "push-up" occurs continually as the radial reaction proceeds. Figure 8 shows how the "height above base" is measured, i.e. from the base to the bottom of the gold wire. The center of the gold wire is thus located at "height above base" plus one half of the gold wire diameter. Figure 9 compares the "height above base" distribution of freshly soldered samples with the same samples aged, and clearly demonstrates the "push-up" during aging. "Height above base" measurements can, as figure 9 demonstrates, be used as a quick measure of the degree of gold to gold-indide conversion.

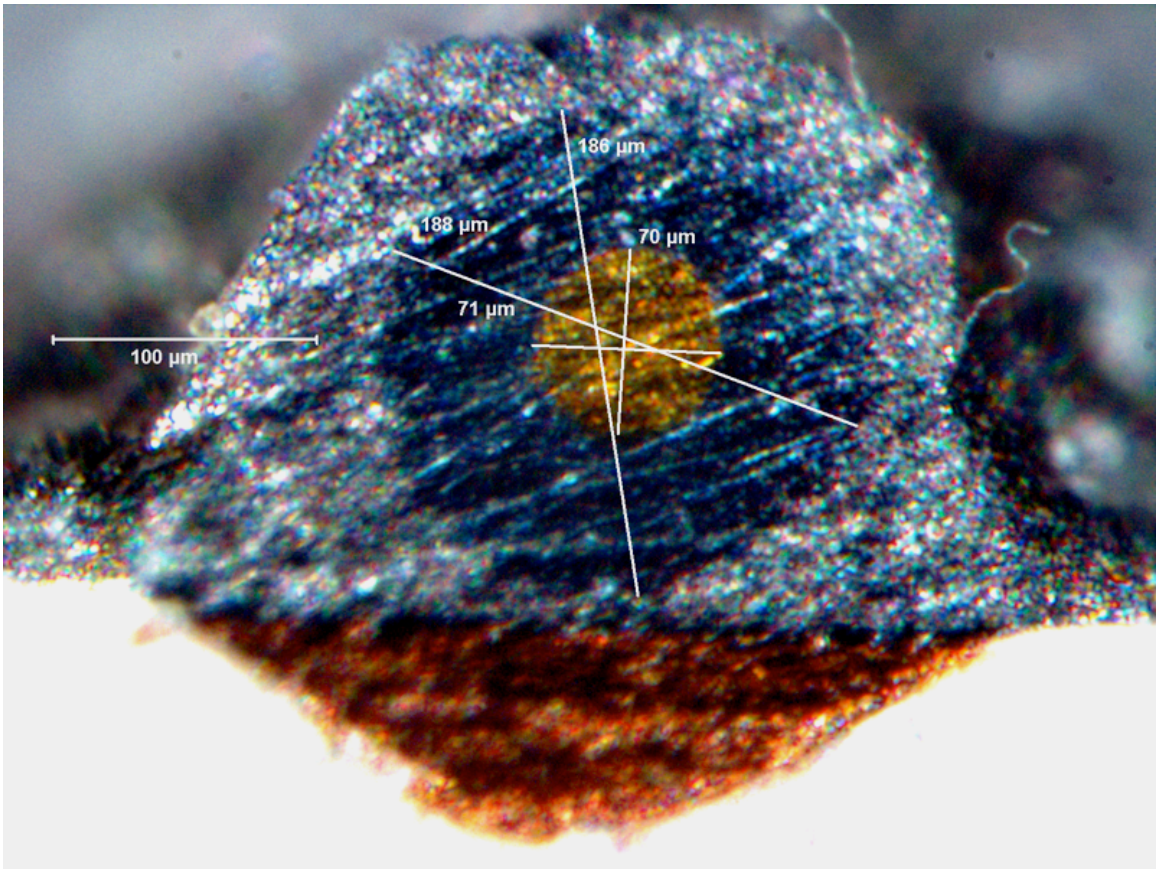

Figure 7. A section through a solder mound holding a partially reacted gold wire of originally 4 mil (101.6 µm) diameter. The center of the wire is "pushed up" from the base by the concentric ring of $AuIn_2$. The remaining gold wire's average diameter is 70.5 µm, and the outer diameter of the $AuIn_2$ ring (black) is 187µm. If the $AuIn_2$ in the ring were fully dense, it would have 4.2 times the volume of the consumed gold (See calculation in table 1). Hence the theoretical outer diameter $D_{AuIn2\ theoretical}$ of the $AuIn_2$ ring is

$$D_{AuIn2\ theoretical} = \sqrt{\{(101.6^2 - 70.5^2)*4.2 - 70.5^2\}} = 132.3\ \mu m$$

Since the measured $AuIn_2$ diameter is 187 µm, it can easily be shown that the $AuIn_2$ has only 50% of theoretical density, even though it is formed under the pressure of having to force all lead and tin out of the way, and deforming the solder mound. (see topview, figure 8.)

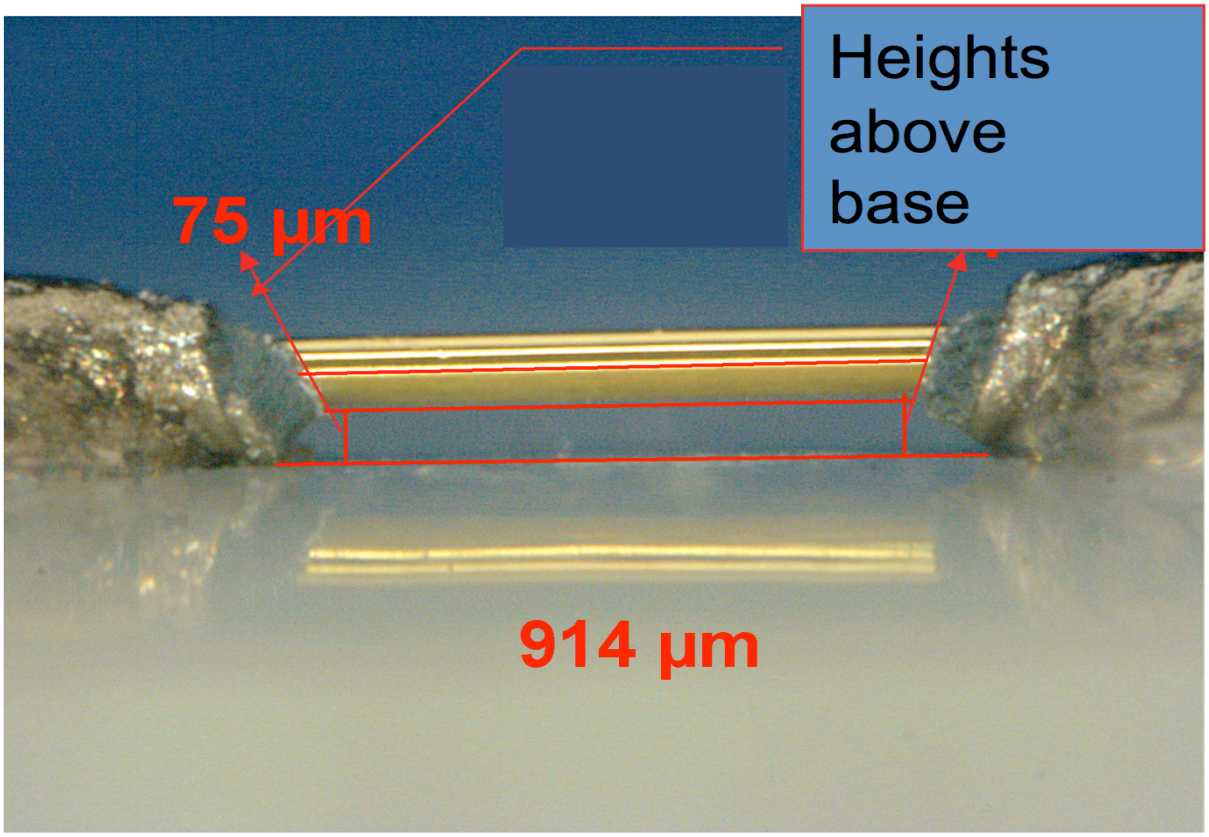

Figure 8. "Height above base" measurement on an aged soldered bridgewire.

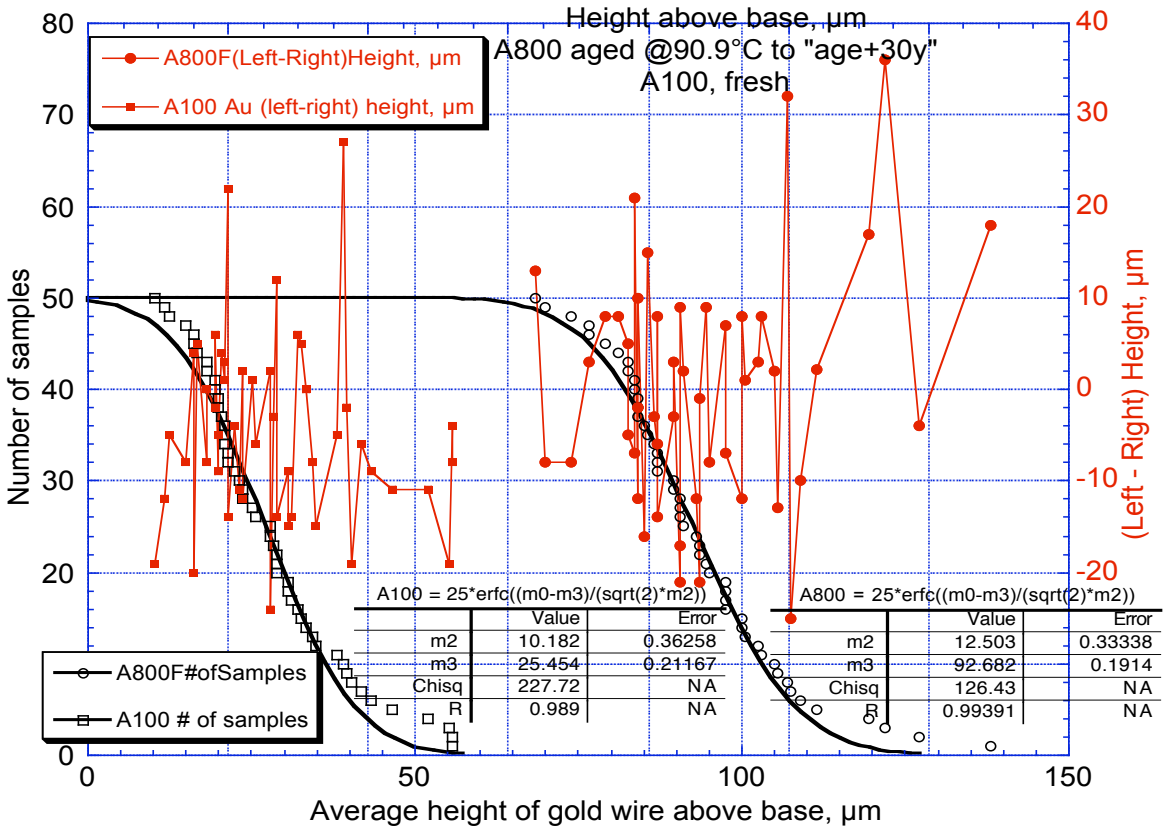

Figure 9. The statistical distribution of "height above base" of a gold wire of 101.6 µm diameter measured before and after aging (black curves) and the difference between the "height above base" at the left and right solder mound (red curves). The bottom of the wire (with an original mean "height above base" of m3=25.45µm, the production specification when soldered) is "pushed up" from the base during aging by the concentric ring of $AuIn_2$ to a mean height m3=92.66 µm. The "ideal" volume (i.e. fully dense, no foreign inclusions, which is NOT correct, see figure 7) of a gold wire fully converted to $AuIn_2$ is 4.2 times its original volume (see Table I), hence the $AuIn_2$ diameter of a gold wire of originally 101.6µm diameter is ~2.05 times 101.6, i.e. 208.2 µm (104.1 µm radius). The center of the aged wire in this graph is located at ["height above base" =92.6 + (.5 gold wire diameter)], i.e. 143.4 µm, ~ 40 µm larger than the $AuIn_2$ radius of a fully converted gold wire. One can thus conclude from the "height above base" measurement, even without sectioning: This gold wire is fully converted.

A.VI.) Summary of the "radial reaction"

We describe the gold-indium reaction in gold-wire bridges soldered with PbSnIn (37.5,37.5,25) as follows: The reaction produces $AuIn_2$ and starts radially inside the solder mound and in time completely converts the gold wire to $AuIn_2$.

We use all literature data available to us to show that this radial reaction proceeds by interface control, i.e. linearly with time, certainly up to a gold consumption of 10µm, and probably by diffusion control, i.e. proportional to square root of time for gold consumption larger than 10µm. We use the data below 10µm gold conversion to develop a "*Linear Reaction Model*" to predict (conservatively) the gold wire consumption in 1.5 mil gold wire headers as a function of time and temperature.

We use surveillance data to demonstrate that the gold consumption rate has a statistical distribution that can be approximately by an error function (-> Gaussian distribution) with a width at half-height of about 10% of the mean value.

We show that the conversion from gold to gold indide "pushes up" the gold wire from its base, and that measurement of this "push-up" can be used as an estimate of the degree of gold conversion inside the solder mound.